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Real Time Monitoring of Photocatalysis:  
An Application and Expansion of the Quartz Crystal Microbalance

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An Honors College Project Presented to  
the Faculty of the Undergraduate  
College of Science and Mathematics  
James Madison University

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by Perrin Michael Godbold  
Department of Chemistry and Biochemistry

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Accepted by the faculty of the Department of Chemistry, James Madison University, in partial fulfillment of the requirements for the Honors College.

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# Real Time Monitoring of Photocatalysis: An Application and Expansion of the Quartz Crystal Microbalance

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*KEYWORDS: Quartz Crystal Microbalance, TiO<sub>2</sub>, Photocatalysis, Nanoparticles, Gas Absorption, Pollutant Destruction*

*Abstract: There are many applications of photocatalytic chemistry, with hundreds of researchers investigating photocatalytic materials. Another method of investigation could aid these researchers and contribute significantly to this field. This study attempts to develop a new method of analysis by expanding the capabilities of the Quartz Crystal Microbalance (QCM) into the realm of photocatalysis. We coated QCM crystals with the stable and well-known photocatalyst, titanium dioxide, and utilized these coated crystals to begin to develop an analysis procedure for our modified instrument. Some indication of the QCM's sensitivity was seen, but the UV irradiation elicited a frequency change independent of the mass changes.*

Photocatalytic reactions are many and diverse.<sup>1-5</sup> Three major applications of photocatalysis are hydrogen fuel production by water splitting,<sup>4</sup> waste water remediation,<sup>6</sup> and the destruction of gas phase pollutants.<sup>5</sup> To be sustainable and economically viable, all require the efficient capture of photons by some stable photocatalytic material. Titanium dioxide (TiO<sub>2</sub>) is a commonly used material for these purposes, either in its pure bulk form or in some enhanced and modified chemical or morphological form.<sup>4-6</sup> Since applications of photocatalysts and in particular TiO<sub>2</sub> are numerous and diverse, it is desirable to develop new methods for studying photocatalytic reactions.

To accomplish this, this study utilizes the quartz crystal microbalance (QCM), an already existing and well-used instrument. Modifying the sensing probe of the balance, the quartz crystal, should enable the instrument to monitor investigate photocatalytic processes. Specifically, the deposition of a photocatalytic material onto the sensing crystal of the QCM would, in theory, allow the QCM to be used to study any photocatalytic reaction which could be absorbed into or on top of the catalyst. Though any photocatalyst could be used,  $\text{TiO}_2$  is chosen for this study because it is inexpensive, well studied and widely used so it serves to illustrate the universal application of this analytical expansion. This is not the first attempt of this type of study.<sup>7-9</sup> *Abe et al.* published a study in 2009 that focused on expanding the detection limit of the QCM (which may very well be necessary for detecting gas phase absorption).<sup>7</sup> However, further studies by the same author on QCM technology could not be found on either scopus.com or scifinder.cas.com. *Hidaka et al.* investigated the degradation of phenol and catechol,<sup>8</sup> and benzoic and salicylic acid<sup>9</sup> in two separate studies utilizing  $\text{TiO}_2$ /QCM technology. These focused on the degradation of pollutants in solution and thus mass changes detected by the QCM were not easily ascribed to the destruction of pollutants. Therefore, these reactions were also monitored by UV-Vis fluorescence.<sup>9,10</sup> We want our system to be able to function as a stand-alone instrument and to have the capability for use in conjunction with other forms of instrumentation such as FT-IR spectroscopy so that the composition of the photoproducts can be coordinated in coordination with the reaction kinetics established by the QCM.

The three main applications of photocatalysis are briefly summarized below, to illustrate this study's practicality.

### *Applications*

Polluted air, according to the European Environmental Agency (EEA), reduces the life expectancy of people in the most polluted cities by about two years. The average effect of air pollution on health is well shown in a map published by the World Health Organization (WHO) placed here in Figure. 1. This figure well demonstrates that air pollution is a global issue though a more immediate concern for urban areas. Even going indoors does not remove one from risk because the typical indoor pollution is comparable to the outdoor levels and in some cases worse because there is the presence of indoor specific particulate and chemical pollutants that simply add to the base atmospheric pollution. Prevention and reduction of emissions at their sources is needed but a holistic solution must also involve large-scale remediation techniques. Various methods have been used to remediate air pollution including absorbents, chemical oxidizers such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and air systems that vent the air elsewhere. Vents are a viable solution for indoor areas but obviously only move the pollutant without solving the issue. Chemical oxidizers must be replenished and can be hazardous to use, and absorbent material must be replaced or cleaned. Both have continued maintenance costs. A possible solution is the use of a photocatalytic contaminant oxidizers (PCOs). When they fully oxidize pollutants there is no toxic waste production (assuming complete oxidation to  $\text{H}_2\text{O}$  and  $\text{CO}_2$ ). Potentially this solution could require no more energy input than the radiation of the sun once solar powered catalysts are well established.<sup>5</sup>

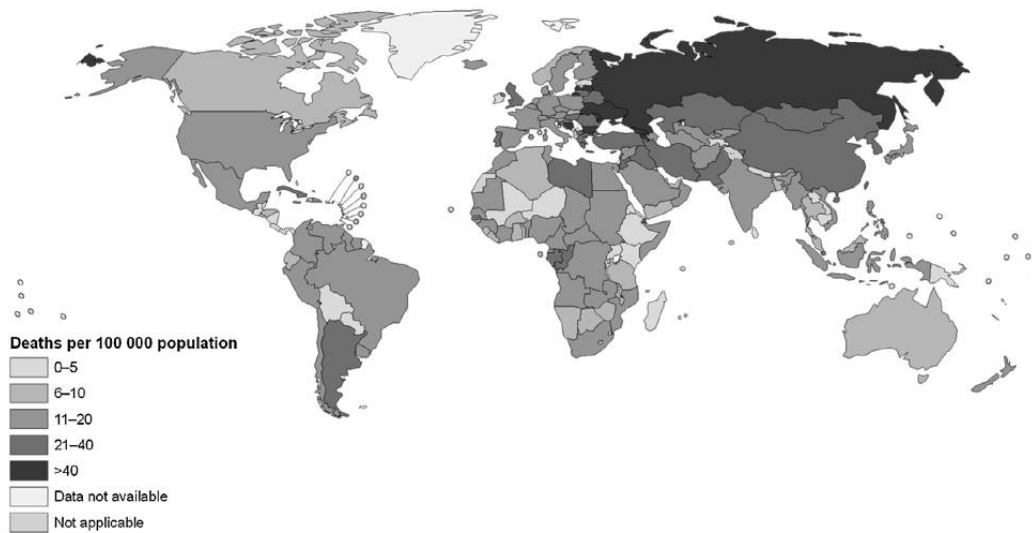


Figure. 1. Map generated by the World Health Organization showing the levels of death per 100,000 people attributed to air pollution.

Water for human consumption and other uses is ubiquitously needed in large quantities. With the global trend of increasing population, the supply of clean, fresh water is increasing the demand for improved methods of purifying waste water. There are a plethora of organic pollutants which can have carcinogenic and toxic effects in even supposedly clean water. Agricultural, industrial, and domestic uses all have specific organic run-off. Organics can be particularly detrimental since their longevity enables them to contaminate ground water and to even spread volatily to other areas. Two particularly large areas of wastewater pollutants are textile and industrial effluents. These destroy stream, lake, and reservoir environments which, besides being bad in and of itself, results in health and monetary costs for societies using these water systems. Most developed countries are able to manage their water remediation but the cost of this sizable infrastructure is not practical for developing

countries.<sup>10</sup> Further, in any water remediation system, there are some organics that defy traditional purification methods and remain in the water; these are called persistent organic pollutants (POPs). Also, most remediation systems deal with organic or inorganic remediation but not both. An effective solution to wastewater remediation would degrade organic pollutants to some benign product and reduce metal contaminants to innocuous complexes. Development of an efficient PCO could be used in conjunction with existing methods of organic removal or as the primary method where no substantial system exists.<sup>6</sup>

An energy application of photocatalysis is the production of hydrogen gas via water splitting. Hydrogen is a desirable alternative fuel because it can have a completely clean and renewable life cycle. Most of the hydrogen currently is produced from hydrocarbons, particularly methane, so it still produces undesirable byproducts. With water splitting via photolysis, hydrogen fuel could become solely generated from water and sunlight. Upon being “burned” only water would be produced, generating energy with no hydrocarbon or greenhouse emissions. Though the technology of hydrogen storage and hydrogen burning engines are not yet cost effective enough to make hydrogen fuel cars economically viable, hydrogen cars do exist and research on hydrogen storage for vehicular applications is in progress. Since hydrogen has a high energy to mass ratio, the hydrogen engine is effective, but its volume to energy ratio is poor; thus, storing hydrogen for commercial use will require advances in metal-organic frameworks (MOFs) and other gas storage applications.<sup>4</sup>

TiO<sub>2</sub> is an ideal photocatalyst for these three broad applications because it is abundant, mass produced, thermally stable, photochemically stable, chemically effective in water, easily activated, and non-toxic. Being abundant and mass produced means it is inexpensive

so it could be applied on the scale required for widespread pollutant remediation. Indeed, the US Department of the Interior and the US Geological Survey reported that in 2013, 6.6 million tons of  $\text{TiO}_2$  was produced globally (1.3 million in the US).<sup>11</sup> Many researchers know the potential of  $\text{TiO}_2$  and have therefore invested their efforts to making it more catalytically active. In fact, on the scientific journal database website Scopus, the search “ $\text{TiO}_2$ ” with the limitation of “photocatalyst” for the years 2016-2017 alone generated over 5000 research articles and 121 review articles. Our study could give these researchers another tool with which to investigate these systems.

#### *Quartz Crystal Microbalance Functionality*

The QCM’s ability to detect minute mass changes is best described by the Sauerbrey Equation, which in its simplest form is:

$$\Delta f = (- C_f)(\Delta m).$$

Where  $\Delta f$  is the observed frequency change in Hz,  $\Delta m$  is the mass change per unit area ( $\text{g}/\text{cm}^2$ ), and  $C_f$  is the sensitivity factor of the particular crystal ( $\text{Hz } \mu\text{g}^{-1} \text{ cm}^2$ ). For the addition of thin films around room temperature with a uniform crystal, the linearity of the Sauerbrey Equation holds. The QCM at its genesis was mostly used as a gas phase mass sensor, but it can be applied to more viscous media such as liquids. The modification of the surface for specific molecular detection, such as substrates and proteins, has been particularly popular. The addition of mass to the crystal surface is assumed to be a rigid film which experiences no shear from oscillation, thus the sensitivity factor remains constant. The sensitivity factor can further be described by the equation:

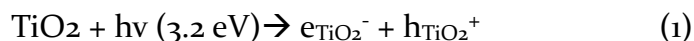


$$C_f = 2(n)(f_o)^2/(\mu_q\rho_q)^{1/2}$$

Where  $n$  is the number of harmonic oscillation,  $f_o$  is the fundamental or base frequency of the crystal,  $\rho_q$  is the density of the quartz [ $2.648 \text{ g cm}^{-3}$ ], and  $\mu_q$  is the shear modulus of the quartz. If the additional film can be assumed to be uniform, the film thickness is equal to the mass change divided by the film material's density or  $T_f = \Delta m/\rho_f$ . An accurate measure of thickness can be obtained for films that change up to 2% of base frequency. Afterward, corrections for the elasticity of the film must be applied. The instrument used in this study is capable of detecting 1.0-0.01 Hz changes corresponding to a gate interval of 1-10 seconds. Overall, the QCM is a versatile and sensitive analytical balance.<sup>12</sup>

### *TiO<sub>2</sub> Photocatalytic Mechanism, Modifications, and Morphologies*

*Mechanism:* As a semiconductor, TiO<sub>2</sub> has an intermediate energy gap between its empty conduction and filled valence bands (CB and VB, respectively) as opposed to the continuous, partially filled conduction band of a conductor or the relatively large band gaps found in an insulator. Therefore in a semiconductor, when an incident photon of the appropriate energy (in the case of TiO<sub>2</sub> a photon of 3.2 eV which comes from the near UV region ( $\lambda \leq 387.5 \text{ nm}$ )), strikes the surface, it excites an electron from the VB to the CB. In the CB, the electron is free to move about the compound and can be picked up by some species and initiate chemistry. There is a positive hole where the electron has left where more chemistry is initiated. Which pathway is more effective depends on the system. A reaction scheme describing this photon absorption is shown below (1).



However, the electron also can relax before it initiates any reaction. This recombination of the electron/hole pair releases heat and/or photons. Recombination is rapid and a major source of inefficiency for TiO<sub>2</sub>. Indeed, preventing this process, or rather extending the life of the electron/hole pair is one primary way to improve photocatalysts. Indeed, the effectiveness of a catalytic system largely depends on its ability to sustain longer lived reactive oxidizing species (ROS) whether these are intermediates or a charge separated surface. Any unrecombined electron-hole pairs can reduce and oxidize molecules that have absorbed onto the TiO<sub>2</sub> surface, respectively.<sup>4, 5</sup>

The VB reaction (oxidation) is primary for air and water pollutant destruction and the CB reaction (reduction) is primary for hydrogen production. It should be noted that TiO<sub>2</sub> is ideal for water splitting because the electrochemical potential of its CB and VB match the energies for the reduction and oxidation of water well. Pollutants are often decomposed by a reactive intermediate (such as HO<sub>2</sub>•, HO•, and O<sub>2</sub>•<sup>-</sup>) that has absorbed the available electron from the conduction band. To split water into H<sub>2</sub> and O<sub>2</sub> effectively, the reduction must be more negative and oxidation more positive than the respective E<sub>H<sub>2</sub>O/H<sub>2</sub></sub> and E<sub>H<sub>2</sub>O/O<sub>2</sub></sub> reaction. The basic mechanism for photocatalysis is shown below in Figure 2.

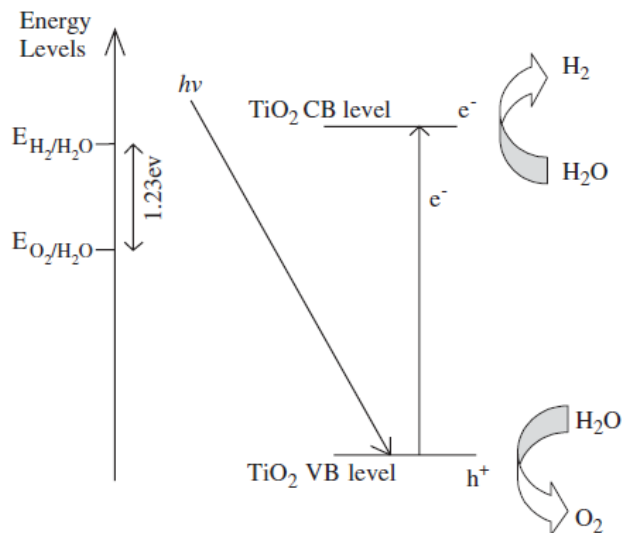


Figure 2. Photocatalytic water splitting upon absorption of an incident photon.<sup>4</sup>

There are three chemical barriers to overcome to improve  $\text{TiO}_2$  to an energy economical photocatalyst.<sup>4</sup> These areas are also where researchers obviously direct their work. First, the mitigation of electron-hole recombination or the extension of their lifetime so that each photon absorb has a better chance of doing the desired chemistry. Second is the prevention of the backward reaction that turns products into reactants. This is of particular concern for water splitting since the recombination of  $\text{H}_2$  and  $\text{O}_2$  into water is an exothermic process. The third is the expansion of the  $\text{TiO}_2$  absorption range into the visible region. By itself,  $\text{TiO}_2$  only absorbs near UV radiation or 4% of the total sunlight available. Thus, most of the sunlight that hits  $\text{TiO}_2$  is either absorb as heat or reflected away. These three inefficiencies apply to all ways that  $\text{TiO}_2$  is photocatalytically utilized. The next section summarizes some of the attempts to improve photocatalytic efficiency, in particular, those for the destruction of gas phase pollutants.<sup>4-6</sup>

*Modifications:* Additives can be paired with  $\text{TiO}_2$  to improve efficiency. These materials broadly fall into two categories: those that are temporary and have to be replaced and those that are combined during the production of the photocatalyst which indefinitely alters it. Organics have been used as an electron bank and have been shown to improve hydrogen production. The organics are oxidized by the positive hole preventing the excited electron from recombining thereby promoting CB chemistry. The organics add hydrogen to the system which is certainly one cause of increased  $\text{H}_2$  production. Four model organics showed the following trend in effectiveness: EDTA > methanol > ethanol > lactic acid. It is not practical to have to continually supply a photocatalyst with organics if the organics must be purchased; however, there is a possibility of combining wastewater remediation with hydrogen production to create a system that treats water while also making a useful product. In general, the use of waste products as hydrogen production fuels is becoming a more active field. Carbonate salts have been reported to reduce the back reaction (recombination of hydrogen and oxygen). The anion of the salt is degraded into  $\text{CO}_2$  and  $\text{O}_2$ . Adding carbonate salts could be economical as they exist in abundance as limestone. The type of cation did affect efficiency but the mechanism is not known. Since many carbonates are common components of many water bodies and especially those with limestone in the area, it is encouraging to know that the salts will aid and not hinder catalysis.<sup>4, 5</sup>

Materials that enhance but are not consumed are largely inorganic. Inorganic materials can serve to temporarily and alternately absorb the VB hole or the CB electron, functioning catalytically rather than destructively. For instance,  $\text{Ce}^{3+}/\text{Ce}^{4+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  pairs have been shown to improve efficiency as the less charged species absorbs a VB hole while water is split

to form oxygen and then return to the lower charged state by absorbing a CB electron to drive water splitting with the production of hydrogen. Nobel metals have been studied and shown to improve efficiency because of their lower Fermi levels by providing a place for the excited electrons to collect and thereby promoting charge separation. Ni and Cu, while not the most effective, may be the most usable because they are not as expensive as Pt or Au.<sup>4-6</sup>

Broadly speaking,  $\text{TiO}_2$  can be doped anionically or cationically to improve efficiency. Anionic doping can increase the absorption range into the visible, utilizing 95% of the spectrum that  $\text{TiO}_2$  would not otherwise use. Cationic doping also broadens the photon absorption spectrum by creating smaller energy gaps. Cationic doping is becoming less popular. The dopant chosen and the abundance of the dopant dictates the doping effectiveness. However, it is worth noting that more absorption does not necessarily mean more catalytic activity.  $\text{TiO}_2$  can even be “self-doped” from thermal decompositions of peroxy- $\text{TiO}_2$  compounds. This creates oxygen vacancies that can act as electron traps. Some of these compounds have been known to be unstable, however.<sup>5</sup>

*Morphology:*  $\text{TiO}_2$  exists in nature in four forms: Anatase, rutile, brookite and monoclinic. Anatase is the most photolytically active while rutile is the most thermodynamically stable. The anatase form is the most commonly used and the one used in this study. In gas phase pollutant destruction, the morphology of the  $\text{TiO}_2$  can dictate how efficient the catalyst, Maximizing absorption and active surface area both improve efficiency. The simplest way to improve surface area is to decrease particle size into the nano-region. Nanoparticles, nanosheet, nanofibers and supported porous structures are all ways to improve absorption.

Figure 3 illustrates the range of morphological form suited to improving gas absorption and destruction.<sup>5</sup>

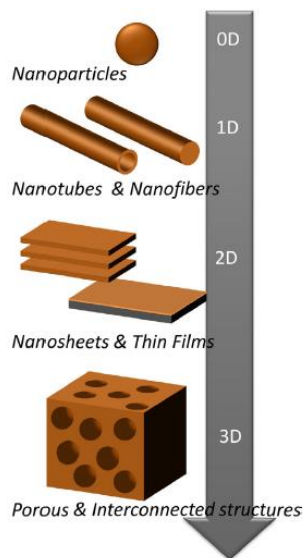


Figure. 3. Dimensionality of  $\text{TiO}_2$  morphologies for gas absorption.

When developing a catalyst for commercial use it must be stable from the air or solution movement in its environment. For instance,  $\text{TiO}_2$  must not be dislodged or blown away. With the considerations outline above, in developing this instrumentation, the goals of this project were threefold: 1) prepare a photocatalytic suspension from literature and effectively and stably coat the gold sensing side of QCM crystals. 2) Test the coated surfaces for photocatalytic activity. 3) Use the catalytically active QCM crystals to detect absorption and degradation (desorption) of organics by measuring mass changes with the QCM.

## *Experimental Methods*

*Suspension Preparation:* Synthesis of the  $\text{TiO}_2$  suspension was carried out similarly to the procedure recorded in *Othman et al.* A 3% by volume PAA aqueous stock solution was made and its pH adjusted to 8.5 with ammonia. Anatase  $\text{TiO}_2$  18 nm particles were used as received from US Research Materials, Inc. Twenty-five grams of  $\text{TiO}_2$  was gradually added to 50 mL of the stock solution while stirring. This suspension was sonicated for 30 minutes to break apart agglomerates and disperse the  $\text{TiO}_2$  in the suspension. Before any later use of suspension, 15 minutes of sonication was applied to disperse the material.

*Coating Surfaces:* Both the benchmark silicon and the QCM gold surfaces were made hydrophilic before the suspension was applied. Silicon wafers were made hydrophilic by induction in a solution of concentrated sulfuric acid and hydrogen peroxide followed by induction in concentrated sodium hydroxide. Gold was made hydrophilic by being placed under 60 seconds of an oxygen plasma at 200 W with the charged plate above and the gold resting on the grounded plate. The coatings were dispersed via spin coating. The suspension was applied to the surface with a disposable dropper, then immediately spun for 1 minute at 2000 or 3000 rpm. The surfaces were then placed on a hot plate for 1 minute to dry any excess water. The topography of the surfaces was measured with a surface profiler and microscopy images were taken with an optical microscope.

The surface profilometer operates by running a stylus with a 2  $\mu\text{m}$  tip a certain “x” distance (1000-5000  $\mu\text{m}$ ) over the surface and while recording the “y” distance or vertical displacement relative to the “x” distance traveled. This provides a mountain and valley

outline of the surface, giving a picture of the uniformity and agglomeration on the surface. On all coatings, a piece of silicon rubber was placed on the approximately 9 cm<sup>2</sup> square silicon wafers before spin coating (and removed after) to give an uncoated benchmark to use as a control when examining the topography. With these benchmarks, the step height or approximate thickness of the coating can accurately be determined. This approximate thickness is then used to help calculate the raw average roughness (RA) and root mean square roughness (RMS). RA is determined by the mean of the difference of each data point and the approximate thickness. RMS indicates how uniform the mountains are and is calculated by the square root of the mean of the squared result of the difference of every data point and the approximate thickness. The data for roughness for the silicon surfaces is derived from 3 measurements each of 2000  $\mu\text{m}$  in length across. Gold surfaces data are derived from 5 measurements each of 5000 microns across.

*Photocatalytic Degradation FT-IR Tests:* Photocatalytic degradation products were discerned by injecting an FT-IR gas cell containing TiO<sub>2</sub> coated surfaces with approximately 10 microliters of model organic and irradiating the cell through the cell's Pyrex walls with an 115 V, longwave UV lamp with no filter for 1-4 hours. Before and after irradiation, the gas cell was placed in a Nicolet FT-IR and the spectrum was obtained from 400 to 4000 cm<sup>-1</sup> by co-adding 32 scans at a resolution of 32 cm<sup>-1</sup>. The cell before injection was used as the background. The chamber was purged with nitrogen for 10-15 minutes before any individual spectrum was taken.



*PAA removal:* Some PAA was removed from the surfaces by a 10-second O<sub>2</sub> plasma run with the same parameters used as for the hydrophilic treatments of gold surfaces.

*QCM Testing:* QCM testing was carried out using a Stanford Research Systems QCM200, with coated 5 MHz crystals. When testing isopropanol, 10 µL of alcohol was dropped with a micropipette directly onto the crystal surface. The QCM probe was placed inside a specially designed chamber pictured below in figure 4. The A's indicate gas inlet and outlets for gas flow, B indicates a sealable opening for a thermocouple to be placed near the wand head, and the C's indicate the UV admissible windows. The lid containing the windows is screwed in place during irradiation tests.

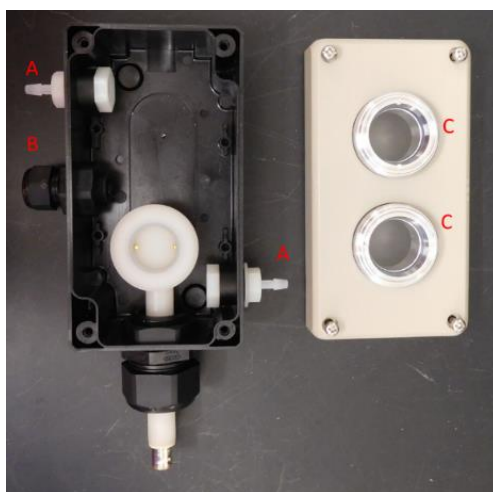


Figure 4. Image of QCM testing chamber.

## *Results and Discussion*

*Surface Coatings on Silicon.* An “effective” coating will be both dispersed and contain few agglomerates. An even coating ensures a more accurate reading from the QCM and the

minimization of agglomerates provides a greater specific surface area to maximize the amount of photochemistry possible relative to the mass of the photocatalytic material and the coated area. Silicon was used as an ideal model surface to study the suspension coatings and their photocatalytic activity. It is ideal because it is easily made hydrophilic, has few surface imperfections, and is inexpensive.

After its hydrophilic treatment, silicon is hydrophilic to the point that not only is there no measurable contact angle from a water droplet, but also the water droplet will remain adhered to the surface when the sample is shaken. This high hydrophilicity should ensure maximum adhesion of the aqueous suspension. The first coating onto silicon was the PAA stock solution, which was applied via spin coating at 3000rpm. After PAA, the  $\text{TiO}_2$ /PAA suspension was coated at 2000 and 3000 rpm onto silicon. The surface profiler was used to gain a basic understanding of the coatings' characteristics. Figure 5 and 6 show the surface profiler graphs of 2000 and 3000 rpm coatings on silicon respectively.

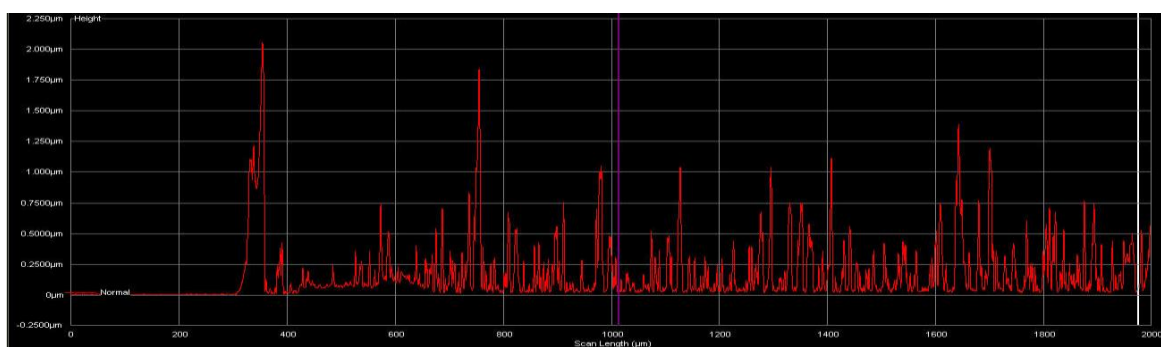


Figure 5. Surface profilometer graph of 2000 rpm  $\text{TiO}_2$ /PAA coating on hydrophilic silicon.

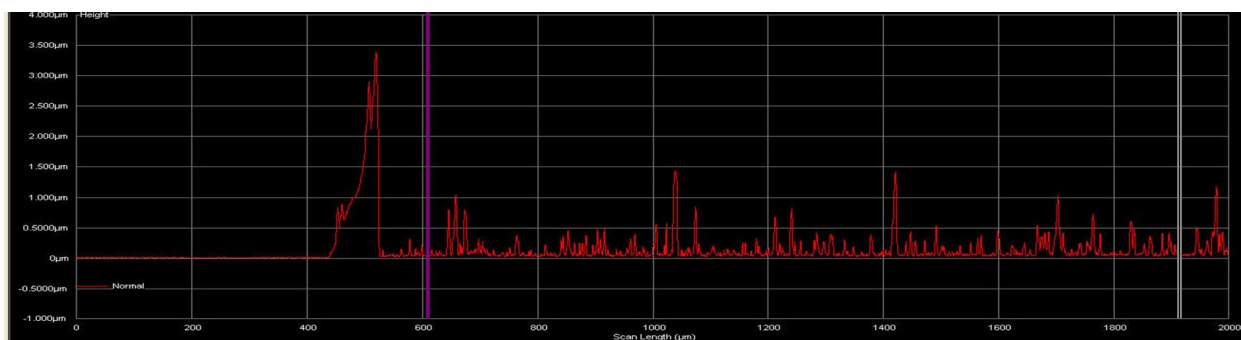


Figure 6. Graph generated by surface profiler of the 3000 rpm TiO<sub>2</sub> coating. The purple and white lines indicate the range over which the RA and RMS calculations were taken.

These figures are representative of profiles taken for silicon. The initial flat line with no y-axis displacement is the stylus moving over the silicon rubber preserved baseline. The first large peak shows where an artificial “snowdrift” of the suspension was pushed up against the silicon rubber during spin coating. After this large peak, the profile shows a more even distribution of “mountains” and “valleys”. Even with sonication and starting with 18 nm particles, agglomerates as large as 1.5 microns for 2000 rpm coatings and 1.75 microns for 3000 rpm coatings are seen. Table 1 summarizes these graphs with thickness, RA roughness, and RMS roughness values.

Table 1. Surface profilometer calculated values for silicon surfaces.

Silicon Surfaces	Average Thickness (nm)	Roughness	
		RA (nm)	RMS (nm)
PAA	39	2	6
TiO <sub>2</sub> (2000 rpm)	181	137	193
TiO <sub>2</sub> (3000 rpm)	128	121	181

There is not a significant difference between the roughness of the 2000 and the 3000 rpm samples. The high hydrophilicity of the surfaces likely controls the agglomeration. Even though there is a significant variance in the thickness of the coatings corresponding to their coating speed, the agglomerations of nanoparticles are approximately similar. However, the 2000 coating was likely was a more thorough coating of the surface as its average thickness is greater. Thus, since their roughness similar, the 2000 rpm “mountains” must be on a “plateau”—similar “mountains” and “valleys” at a greater average height.

The RAs indicate that there are many agglomerates approaching the micrometer scale. The RMS indicates that the dispersion of the agglomerates is not uniform. In other words, there are both small and big mountains. Additionally, there are also many places not coated with particles as the profile shows a baseline that drops almost back to zero. However, these coating while not exactly nanoscale, cover the surface and, with some variability, are dispersed. Finally, the stock solution of PAA coated in an even thin layer with a minimal step height, RA, and RMS. Therefore, it is assumed that the nanoparticles rest embedded in a layer of PAA. It is not known whether or to what extent the PAA covers the nanoparticles.

*Surface Coatings on Gold QCM Crystals:* Gold is not able to be made hydrophilic via sulfuric acid and hydrogen peroxide as silicon is. In the literature, there are ways to create a hydrophilic gold surface by applying self-assembling monolayers (SAMs). However, not wishing to modify the surface before applying the suspension, we attempted to functionalize the surface by submitting the QCM crystals to an oxygen plasma for one minute. A

subsequent water droplet test showed an unmeasurable contact angle similar to silicon, though the hydrophilicity was not as strong since the applied water droplet could be shaken off. The same methods of spin coating and surface profilometry as had been used for silicon were used here. However, since it is desirable to have the entire surface coated to maximize reactant absorption, silica rubber was not used to preserve a baseline. Instead, an artificial baseline was created by wiping a small part of the gold clean post-coating with a damp cotton swab as seen in the microscopy image in Figure 7.

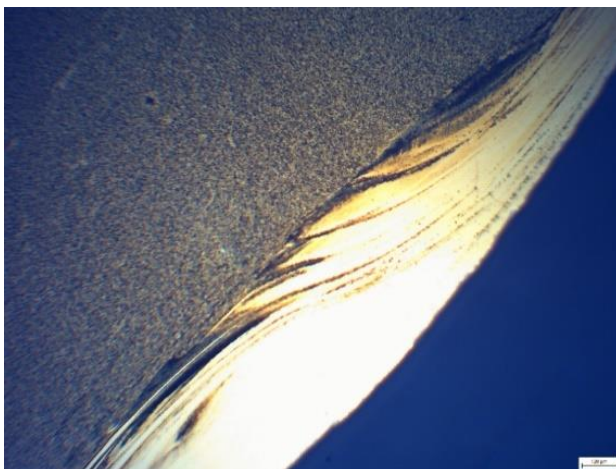


Figure 7. Microscopy image of the edge of a coated QCM crystal that has been wiped with a cotton swab to create an artificial baseline.

Figures 8 and 9 show the 2000 and 3000 rpm coatings on QCM crystal gold, respectively. The profile has sharper “mountains” than the silicon surfaces and there are several large agglomerates from each coating approaching 5  $\mu\text{m}$ . The average thickness, RA, and RMS are listed in Table 2. As seen with silicon, the spin speed clearly affected the average thickness of the coatings with the lower spin higher spin speed typically giving a thinner coating. The

RA and RMS are larger than those found for silicon, which we assumed from the graphs. The differences of roughness are attributed to the difference of hydrophilicity of the surfaces. With less attraction to the gold surface, the nanoparticles agglomerated together to decrease their surface area which is often more energetically favorable. The RMS indicates a greater range of particle size distribution which is in part due to the largest agglomerates increasing from 1.5 to 5 microns.

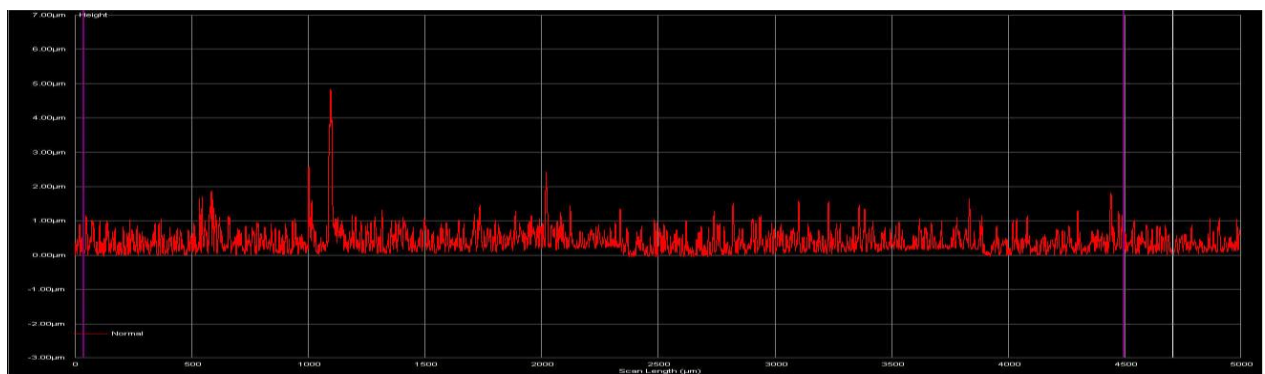


Figure 8. Surface profilometer graph of a 2000 rpm coating on QCM gold over 5000  $\mu\text{m}$ .

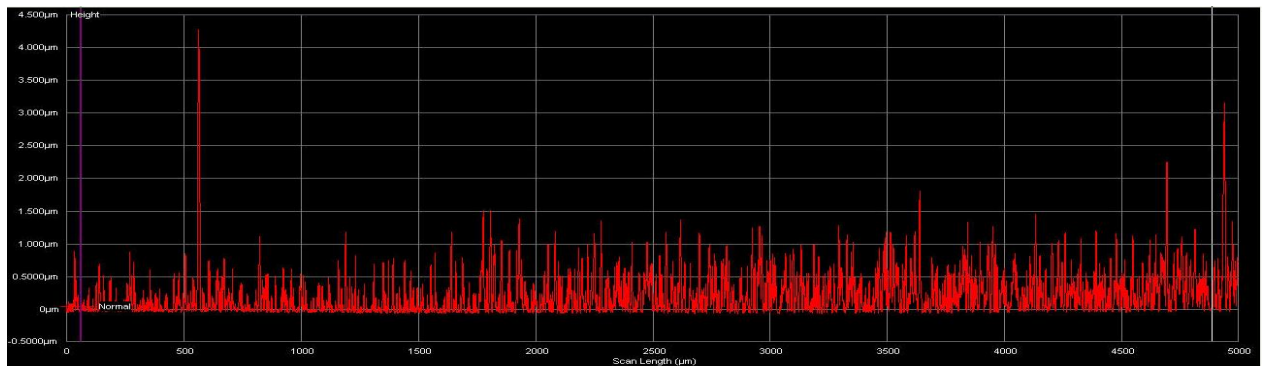


Figure 9. Surface profilometer graph of a 3000 rpm  $\text{TiO}_2/\text{PAA}$  coating on QCM gold.

Table 2. Thickness and roughness data for suspension spin coatings on QCM crystals.

Gold QCM Crystals	Spin Speed (RPM)	Average Thickness (nm)	Roughness	
			RA (nm)	RMS (nm)
1	2000	409	242	314
2	3000	134	148	202
3	3000	202	185	253

Interestingly, there was also variance in sizes between the 3000 rpm coatings. We attribute this to the suspension. The suspension settles over time in agreement with the literature,<sup>12</sup> and even with stirring and sonicating the suspension before coating there is still a gradient of particle concentration. Since the applied droplets of suspension were not extracted from the same depth, different concentrations of  $\text{TiO}_2$  for the same volume were applied. Even if the concentration gradient was minimal, the amount of dropped suspension was not kept consistent—poorly planned in retrospect. Also, agglomeration likely increases with time and since the coatings were not spun on the same day, the later coatings had larger agglomerates because the starting suspension had larger starting particles. Though the coatings are not ideal, the coatings should still be catalytically active.

Microscopy images of coatings on the QCM gold were taken with an optical microscope for a range of resolutions (40-600 times magnification). Figure 10. shows images increasing in resolution left to right. They show an even dispersion of agglomerated particles. (They must be agglomerated because 18 nm is not resolvable with an optical microscope). As the resolution increases the smallest resolvable fundamental unit seems to be spherical. Thus, the larger “mountains” detected by the surface profiler are agglomerates of agglomerates as shown by the image on the far right in figure 10.

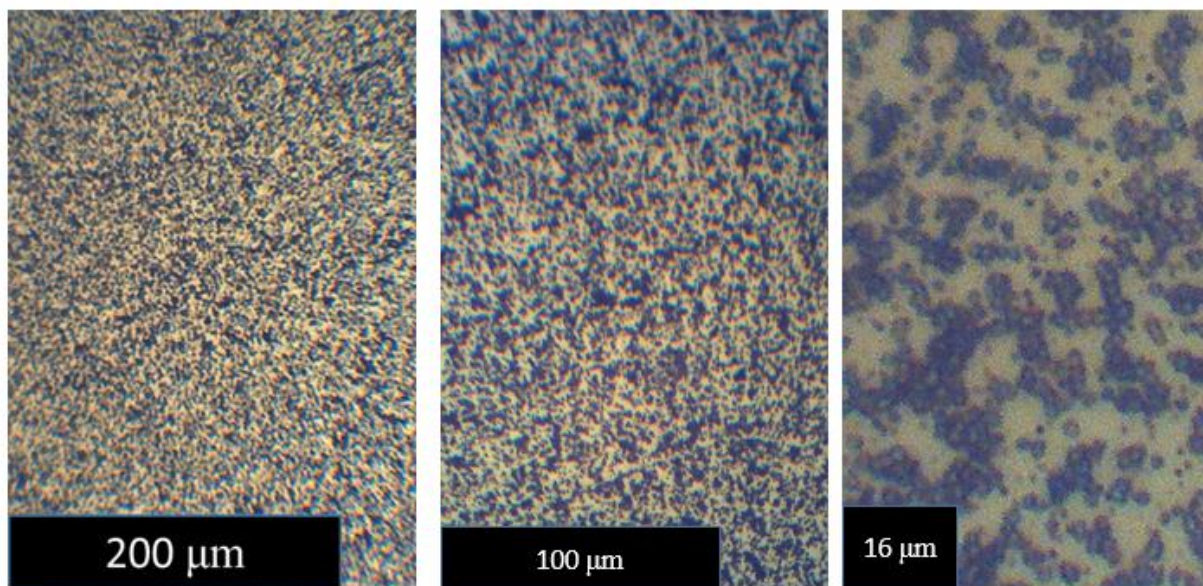


Figure. 10. Microscopy images of 2000 rpm coated QCM gold.

### *Photo-degradation*

Isopropanol was used as an model organic to test the photocatalytic activity of the coated surfaces. The coated silica squares were broken into three rectangles and placed in an FT-IR gas flow cell. The background for all runs was taken in a nitrogen flushed chamber with the gas cell as part of the background. The background spectrum is shown in Figure 11. Note the absorption of the windows at wavenumber ( $\text{cm}^{-1}$ ) and the presence of atmospheric levels of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .



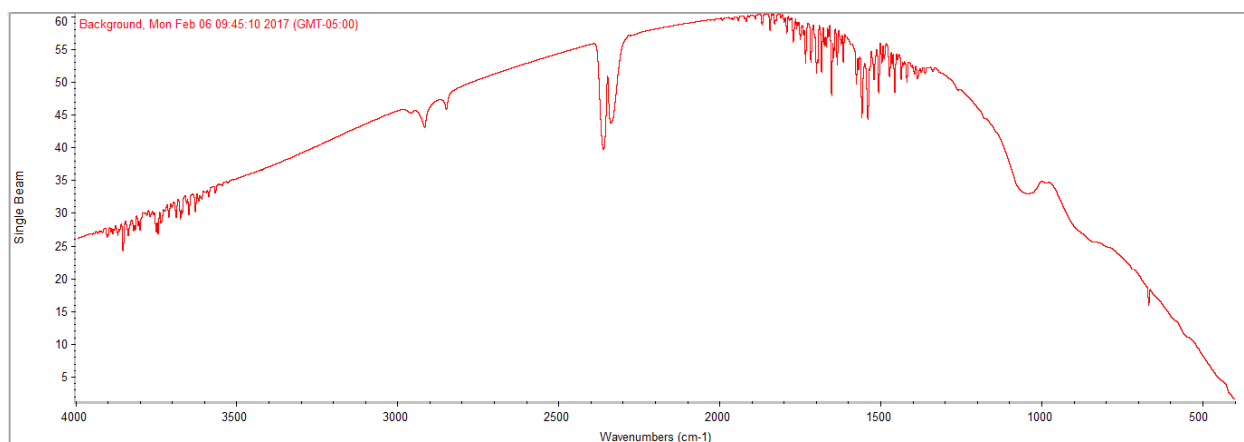


Figure 11. Background spectra typical of the gas cell before isopropanol injection.

Isopropanol was then injected through a septum on the flow cell. The amount injected was not consistent but was around 10 microliters. A spectrum was taken before each irradiation (BI). The surfaces were then irradiated through the wall of the gas cell and then the post-irradiation spectra (PI) were taken. The PI and BI of a one-hour irradiation are compared in Figure 12. The concentration of isopropanol decreased slightly. To determine if there are any products formed, a difference spectrum was obtained by subtracting the pre-photolysis spectrum from the post photolysis spectrum. The resulting spectrum is shown in figure 13. Three things are noticeable from the subtraction result. First, some isopropanol has been lost as shown by the negative peak near  $3000\text{ cm}^{-1}$  and the negative peaks between  $1550$  and  $900\text{ cm}^{-1}$  (A). Referring to the spectra in Figure 12, assures us that those are indeed characteristic isopropanol peaks. Second, there is also an appearance of four peaks between  $1800$  and  $1100\text{ cm}^{-1}$  which are characteristic of acetone (B). Third,  $\text{CO}_2$  (C) has increased and water appears in the spectrum (the highly branched peaks farthest downfield and surrounding the acetone peaks) that was likely made by the photodecomposition. However,

since the humidity of rooms can be variable and water vapor can cling to the walls of equipment it is harder to say if the reaction specifically generated water. Since all spectra were allowed to flush with nitrogen for an extended time (15 minutes), water and carbon dioxide are likely to be products of photolysis. Carbon dioxide is the most stable final product of any photo organic destruction. Acetone is a reasonable intermediate for the destruction of isopropanol as it is simply the oxidized version of isopropanol. These products are a clear confirmation of photocatalytic activity.

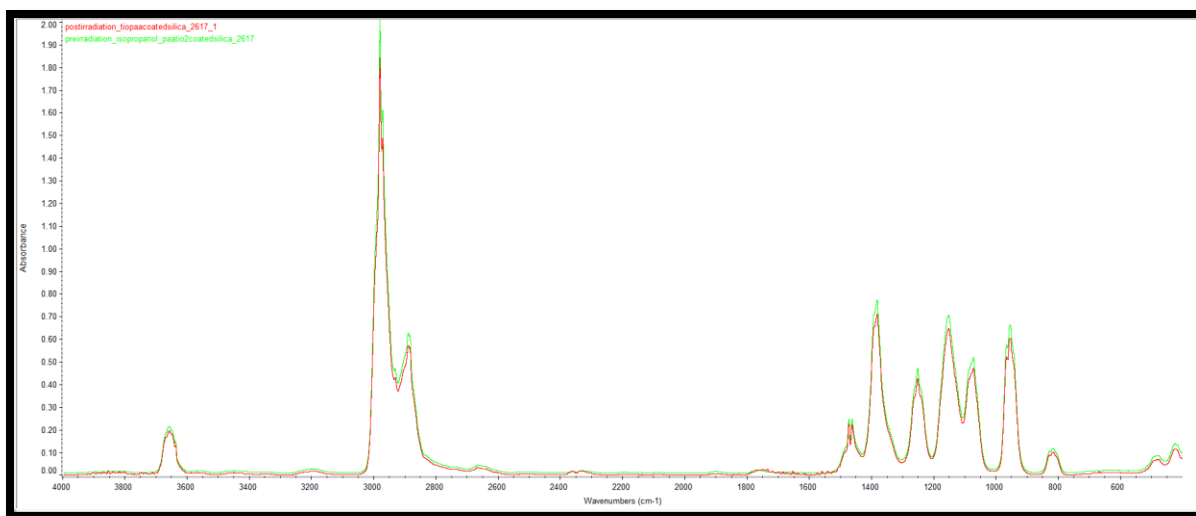


Figure 12. Comparison of BI and PI of isopropanol for a 1-hour irradiation. The green spectrum is BI and the red spectrum is PI.

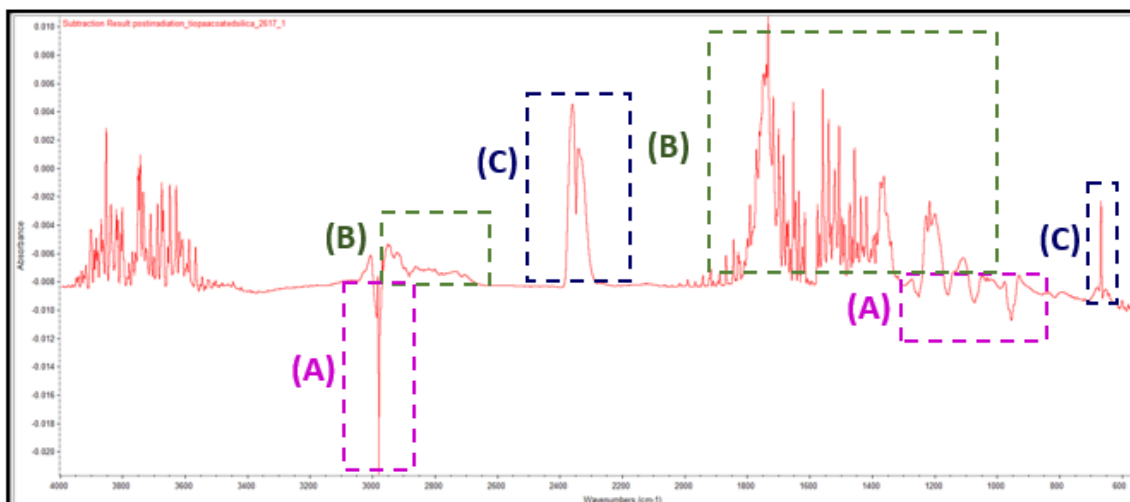
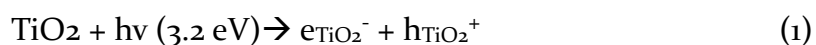


Figure 13. Spectra generated from the subtraction result of BI and PI which are depicted in figure 12.

Though we have not elucidated the specific pathway of degradation, the general pathway has been shown in the literature. The flowing series of equations outlines a typical photosystem's pathway.<sup>11</sup>



Though it is possible our system operates differently, we see the final products of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . The “other products” in our system, because it is closed, simply run through the

reaction(s) again until everything in our cell has been degraded to the most stable products,  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .

*Catalytic Efficiency:* While development of a better catalyst is not the goal of this project, having a more efficient catalyst would aid in mass change detection simply by increasing the rate of mass change. As seen in Figure 12, an hour of irradiation does not produce a considerable change in alcohol concentration. (Absorption and concentration are linear when below the chamber is below saturation). The PAA seems to adequately fulfill its purpose as a dispersant and glue; however, it could also be inhibiting the activity of  $\text{TiO}_2$ . We hypothesized that the PAA might be covering the  $\text{TiO}_2$  and preventing isopropanol from reaching the catalytic sites on the  $\text{TiO}_2$ . To remove some PAA, the silica surfaces were run under a short oxygen plasma and then the irradiation test was run again to determine if the activity had changed. Figure 14. compares a 1-hour irradiation of non- $\text{O}_2$  treated surface (PAA present) with one treated by the oxygen plasma (some PAA removed). The absorbance of isopropanol for the non-treated surfaces changed by 0.021 and on the treated surfaces change by 0.119 under after an hour of irradiation. This is nearly a 6 fold improvement for the  $\text{O}_2$  treated surfaces. Our system is not controlled enough to claim this as a precise degree of change. Yet an indication of 6x increased efficiency was quite enough to convince us that removing some amount of PAA was beneficial, and for us to run the rest of our surfaces through a short oxygen plasma to give them the same enhancement. Different times were not tested to find optimal PAA removal, but there should exist a state where physical

stability of the nanoparticles and catalytic activity are appropriately maximized, assuming nanoparticle stability is a function of the amount of PAA co-deposited on the surface.

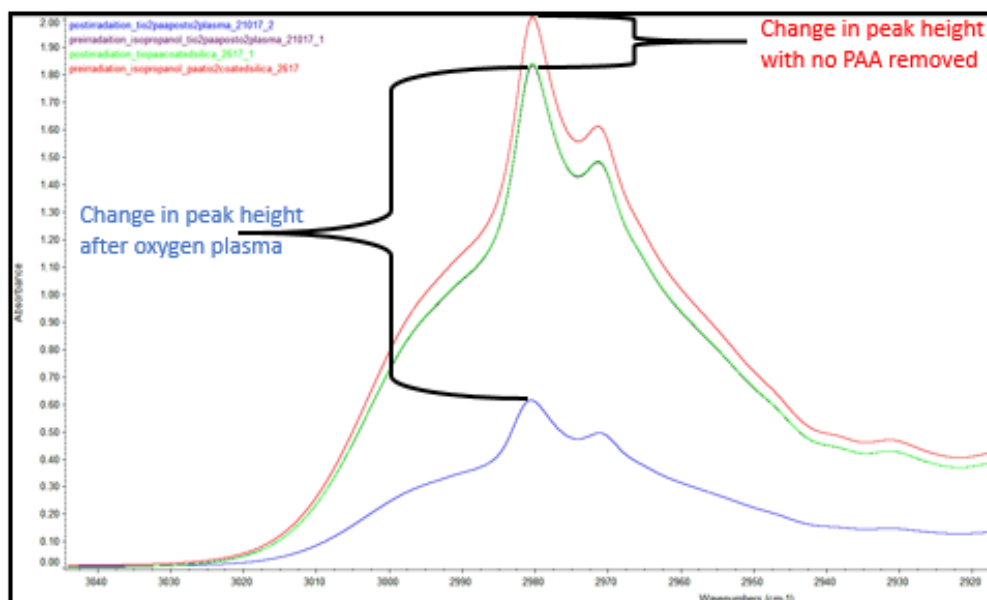


Figure 14. Comparison of catalytic activity of the same surface before and after PAA removal.

### Full system

*QCM Response to UV:* Our full system represents the greatest area of further work. To date, we have done nothing more than confirm the literature for our system. We have run two tests that direct future work. 1) The QCM having piezoelectric quality responds to UV irradiation independent of mass changes.<sup>8</sup> Figure 15 shows the responses of the QCM upon initiation and secession of UV irradiation. Using a coated crystal, the QCM system was first allowed to come to equilibrium (0-1080 sec). The UV light was then turned on. The frequency increased even with no mass changes. The frequency peaked, and then slowly

descended to a new elevated equilibrium. Upon cessation of the irradiation at 2350 sec, and the frequency dropped sharply and then slowly rose towards an equilibrium above the original baseline. Note that in figure 15, it has not yet reached its equilibrium but is nearing it. The elevated higher equilibrium could indicate that material on the crystal was removed during UV irradiation. Similar behavior is seen with an uncoated crystal; however, the last equilibrium was not as high above the before irradiation equilibrium. Thus, some of the effects are possibly from the UV light influence and others from the removal of material. To see if the QCM could detect the removal of small amounts of alcohol, the following experiment was conducted.

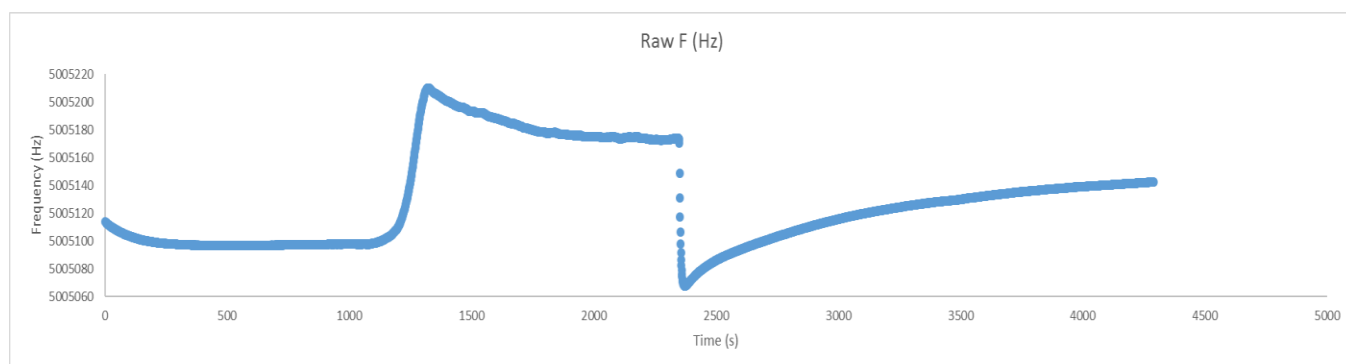


Figure 15. Coated QCM Crystals response to UV irradiation

*Irradiation of Residual Alcohol:* Figure 16 shows the QCM frequency for the following proof of concept experiment. As above, the QCM system was allowed to come to equilibrium. Then 10  $\mu\text{L}$  of isopropanol were dropped onto the coated crystal surface. The viscosity change induced a dramatic frequency decrease. (Note that the decrease is great enough to render the follow frequency shifts poorly discernable so the y-axis has been artificially shortened and removed some data points.) Shortly after isopropanol droplet, nitrogen was

flushed into the system, causing a dramatic frequency increase, presumably from alcohol removal. Under nitrogen gas flow the system was allowed to equilibrate and then the nitrogen was turned off and another equilibrium reached. This equilibrium was determined to be the “dry crystal” with minimal amounts of isopropanol remaining. The UV light was then turned on and left to irradiate to an equilibrium and then turned off. The system was left until equilibrium was again reached. This final equilibrium was 33 Hz greater than the “dry crystal” equilibrium, indicating that the UV lamp likely removed trace amounts of alcohol from the surface. This gives some hope to the possibility of detecting gas absorption from other volatile organics. However, the response of the UV light still must be accounted for. This is a goal of future research.

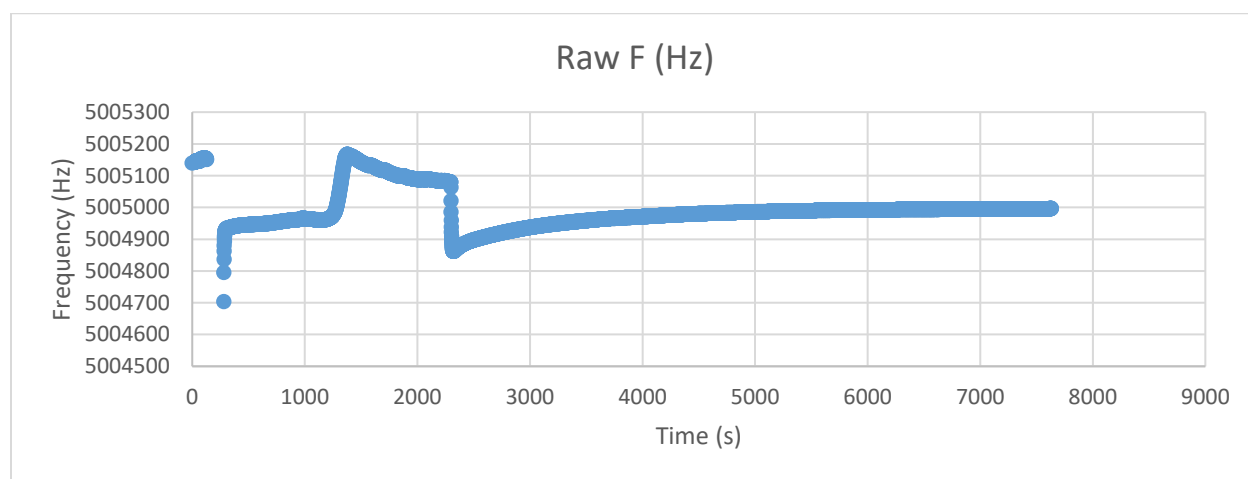


Figure 16. QCM response to the addition of isopropanol with subsequent UV irradiation.

### *Conclusions*

In the process of developing a mass sensitive photocatalytic technology, we successfully synthesized a suspension of  $\text{TiO}_2$  particles and coated QCM crystals with this suspension.

Our coatings did show some considerable agglomeration yet still successfully degraded our model organic. We successfully and easily made gold hydrophilic by use of an oxygen plasma to receive our suspension. Our full system seems to be capable of detecting some layers of alcohol even after leaving the crystal in a drying environment. However, with the effects of the UV light on the QCM's behavior, we were not able to isolate the mass change from photodegradation and thus were unable to determine reaction kinetics. Our future work will endeavor to resolve this problem to achieve effective detection of photolyzed reactions.

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